

ANALYSIS OF UPGRADED SRC-II AND H-COAL LIQUID PRODUCTS

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INTRODUCTION

Interest in catalytic hydroprocessing of coal-derived liquids has intensified in recent times because of the need to convert heavy feeds to more useful fuels for transportation use. Analytical data on upgraded liquids, relevant to physical and chemical characteristics such as specific gravity, aniline point, heteroatom content (O + N + S), etc., are of importance in determining the process parameters which control the product composition and product properties. The purpose of this study was to analyze the upgraded SRC-II and H-coal liquids, provided by the Chevron Research Co., by IR, NMR, GC, GC/MS, and silica gel chromatography, as a function of contact time, with the hope of obtaining a better understanding of coal-liquid refining processes.

EXPERIMENTAL

SRC-II process products were made from Pittsburgh Seam (Blacksville No. 2 Mine) at Pittsburgh and Midway Coal Co. These products were blended in the ratio recommended by the DOE Technical Project Officer to represent a typical net whole liquid product from the SRC-II process at Chevron. The blend is referred to as SRC-II syncrude. H-coal process products derived from Illinois No. 6 were blended in the ratio recommended by Hydrocarbon Research Inc. to represent a net whole liquid process product from the H-coal process at Chevron, and the blend is referred to as H-coal syncrude.

Two samples of SRC-II syncrude and three samples of H-coal syncrude were hydrotreated using Chevron's ICR 106 catalyst (containing nickel, tungsten, silica and alumina) at 750°F and approximately 2,300 psia H_2 partial pressure. The recycle gas rate was roughly 15,000 SCF/B (standard cubic foot per barrel) for the SRC-II runs and 8,000 SCF/B for the H-coal runs.

NMR spectra were obtained with a 600 MHz NMR spectrometer or a 60 MHz FT-NMR (Hitachi Perkin-Elmer) spectrometer with TMS as the internal reference. IR spectra were recorded from neat samples in NaCl plates as thin films on a Beckman IR-20 infrared spectrometer. GC profiles were obtained with a Hewlett-Packard Model 5700A equipped with a flame ionization detector and Sigma-10 data system. Capillary methyl silicone (length 12 m) and methyl phenyl silicone (length 30 m) columns were used. The GC/MS analysis was performed on a sp-2100 fused silica capillary column (length 50 m) interfaced directly into a Hewlett-Packard 5982 MS at 70 eV.

The neutral fractions of the coal-derived liquids were obtained by treating the SRC-II and H-coal syncrudes with IRA-904 anion-exchange resin and then with Amberlyst-15 cation-exchange resin to remove acid and base fractions, respectively. The ion-exchange resins were purchased from Rohm and Haas and were activated according to the method described by Jewell, et al. (1) The neutral fractions and the upgraded coal-derived liquids were separated into saturate, aromatic-I and aromatic-II fractions by silica gel

chromatography. The procedure used involved packing a 1.2 x 105 cm column with 64 g of silica gel which had been activated by heating for 16 h at 80°C in a vacuum oven. A 2 g quantity of the neutral fraction or upgraded liquid was dissolved in pentane and charged to the column. The saturate fraction was eluted with pentane, until the uv absorbance of the eluate at 270 nm equalled 0.05. Aromatic-I and aromatic-II fractions were eluted with CHCl_3 and methanol, respectively, until the uv absorbance at 270 nm reached about zero.

RESULTS AND DISCUSSION

The hydroprocessing conditions, elemental analysis and physical properties of the feeds and upgraded liquids are listed in Table 1. Apparently, the type of coal and contact time greatly influence these properties. The contact time is the reciprocal of the liquid hourly space velocity (LHSV, in $\text{cm}^3 \text{ feed/h cm}^3 \text{ catalyst}$).

Infrared spectra of the coal-derived liquids, before and after upgrading, show distinctive difference in aliphatic stretching bands at 2,920 and 2,960 cm^{-1} of CH_2 and CH_3 , respectively, and aromatic C-C and/or hydrogen-bonded carbonyl stretching at 1,610 cm^{-1} . The aromatic stretching at 3,020 cm^{-1} decreases with the severity (decrease in LHSV) of hydro-treating. The syncrudes show an obvious broad peak centered at 3,400 cm^{-1} which is ascribed to the hydrogen-bonded OH and NH structure. However, a negligible hydrogen-bonded structure was found in upgraded liquids. The neutral fraction, an acid- and base-free fraction, shows similar absorption as the upgraded samples.

NMR spectra show that the aromatic protons decrease with decrease in LHSV (increasing severity of hydroprocessing). The aromatic protons of upgraded coal liquids appearing in the range 6.5 to 7.2 ppm indicate that the upgraded coal liquids contain mostly one to two rings of aromatics. The sharp singlet at about 1.44 ppm is due to cyclohexane which indicates that the content of naphthenes in both the SRC-II and H-coal upgraded liquids is appreciable. This is consistent with the result, Table 1, that the naphthenes are in the range from 57.2 to 89.9% (liquid volume %).

The proton distribution of the syncrudes and their upgraded liquids is listed in Table 2. It is seen that the aromatic hydrogen content decreases with increase in contact time, and the bulk of the aliphatic hydrogens occur at the position β on further away from the aromatic ring, H_β or H_γ , accompanied by decrease in H_α . The increase of H_β in upgraded liquids is primarily due to the increase of naphthene content.

The viscosity of syncrudes and their upgraded liquids was measured by using an Ostwald type viscometer at 298 K. Since the contents of heteroatoms are in the range of only a few ppm and the hydrogen-bonded structure is negligible, the upgraded liquids therefore all have low viscosity, ranging only from 1.25 to 1.40 cp, even though there is wide variation of the saturate and aromatic contents.

In order to characterize the composition of the upgraded samples, silica gel chromatography was employed to separate the coal liquids into saturate and aromatic fractions, and the content of each fraction is listed in Table 3. It is seen that the saturate fraction content increases with contact

time, accompanied by a decrease in aromatic fractions. The neat IR spectrum of the saturate fraction derived from 1.0 LHSV H-coal shows the absence of absorptions at $3,020\text{--}3,080\text{ cm}^{-1}$ and $1,600\text{ cm}^{-1}$, indicating that the saturates are not contaminated by aromatic fractions. This fact is also confirmed by GC/MS analysis of the fractions. The recoveries range between 94 and 99.8%, indicating that the method used for separation of upgraded coal liquids is appropriate.

The saturate and aromatic-I fractions were studied by GC using methyl silicone and methyl phenyl silicone capillary columns, respectively. The temperature programs used for saturate and aromatic-I are from 20°C (2 min.) to 160°C (4 min.) by increasing rate at 2°C per minute, and from 70° to 270°C by increasing rate at 2°C per minute, respectively. The severity of hydrotreating seems not to affect the types, only the concentrations of compounds in both the saturate and aromatic-I fractions. The quantitative analysis of aromatic compounds based on ring-number, by using naphthalene and phenanthrene as internal standards, is listed in Table 4. The more severely upgraded coal liquids contain more 1-ring and less 3-ring aromatic compounds, compared to the syncrude and the less severely upgraded coal liquids.

We have obtained GC/MS chromatograms of the saturate fraction and the aromatic-I fraction of upgraded SRC-II and H-coal. Figure 1 gives the chromatograms for the saturate fractions of upgraded SRC-II and H-coal (both 1.5 LHSV). By matching retention times and mass spectra of the numbered peaks, we observe a remarkable similarity for each fraction irrespective of whether the source is SRC-II or H-coal. Only the heavier end of the aromatic-I fraction is noticeably different. In comparing the chromatograms of Figure 1, the concentrations of the following species are greater in SRC-II than in H-coal: C_6 -cyclohexanes, C_7 -cyclohexanes, C_8 -cyclohexanes, dimethyl decahydronaphthalene, n-decane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, whereas the H-coal saturate fraction contains greater concentrations of the following: C_5 -cyclohexanes, C_4 -cyclohexanes, C_3 -cyclohexanes, and trans-hexahydroindane. In comparing the GC/MS chromatograms of the aromatic-I fractions of H-coal (LHSV 1.0) and of SRC-II (LHSV 1.5), the concentrations of the following species are greater in H-coal than in SRC-II: C_3 -benzenes; C_4 -benzenes, C_5 -benzenes, C_6 -benzenes (C_6 -indane or C_6 -tetralin), indane, and methyl indane. The concentration of C_6 -benzenes is greater in SRC-II (LHSV 1.5) than in H-coal (LHSV 1.0) aromatic-I fractions.

600 MHz PMR spectra of the upgraded SRC-II and H-coal liquids (both 1.5 LHSV) look identical. We have applied the NMR difference technique (2) to obtain differences in concentration of certain species between the two liquids. The difference spectrum was obtained from the individual proton spectra recorded under the same concentration in CDCl_3 and operational conditions. The upgraded SRC-II liquid contains larger amounts of compounds which have CH_2 or CH groups α to the aromatic rings, in addition or in excess to compounds present in the upgraded H-coal liquid.

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TABLE 1. Properties and Analysis of SRC-II and H-Coal Syncrudes and Their Upgraded Liquids*

Feed Sources Processing Conditions	SRC-II			H-coal			
	Syncrude	LHSV, h ⁻¹		Syncrude	LHSV, h ⁻¹		
		1.5	0.5		1.5	1.0	0.5
Specific gravity, °API	18.6	34.1	39.3	25.8	33.1	35.9	36.2
Viscosity (cP) 298°K	2.74	1.25	1.25	2.04	1.40	1.34	1.39
Aniline point, °F	<30	67.5	116.9	<32	75.7	101.3	110.5
Total nitrogen, ppm	8,500	20	0.25	4,600	11.6	1.1	0.5
Oxygen, ppm	37,900	630	40	18,000	160	110	120
Sulfur, ppm	2,900	5	5	3,200	16	51 (?)	8.4
Hydrogen, wt. %	10.46	12.4	13.7	11.39	12.3	12.8	13.2
Carbon, wt. %	86.41			86.96			
Group type, LV %							
Paraffins		7.8	6.4		3.3	2.8	2.7
Naphthenes		57.2	89.9		58.6	73.2	84.0
Aromatics		35.0	4.3		38.1	23.0	13.2

*Received from Chevron Research Co.

TABLE 2. Proton Distribution of Coal Liquids (Area %)

		<u>H_a (9-5 ppm)</u>	<u>H_α (4-2 ppm)</u>	<u>H_β (2-1.1 ppm)</u>	<u>H_γ (1.1-0.3 ppm)</u>
SRC-II	Syncrude	25.28	24.94	31.63	18.14
SRC-II	1.5 LHSV	8.52	13.74	47.92	29.82
SRC-II	0.5 LHSV	3.33	3.22	54.94	38.52
H-coal	Syncrude	15.99	20.58	41.26	22.17
H-coal	1.5 LHSV	7.85	13.01	49.03	30.11
H-coal	1.0 LHSV	5.56	8.79	55.62	30.03
H-coal	0.5 LHSV	4.81	7.48	54.70	33.01

TABLE 3. Composition of Coal Liquids (Wt. %)

		<u>Saturate</u>	<u>Aromatic-I</u>	<u>Aromatic-II</u>	<u>Recovery</u>
SRC-II	Syncrude	15.1	80.2	4.0	99.3
SRC-II	1.5 LHSV	50.6	44.9	1.0	96.5
SRC-II	0.5 LHSV	92.9	5.1	0.8	98.8
H-coal	Syncrude	28.8	66.3	3.7	99.8
H-coal	1.5 LHSV	53.2	30.6	15.6	99.6
H-coal	1.0 LHSV	68.0	23.3	2.7	94.0
H-coal	0.5 LHSV	73.8	22.0	3.4	99.2

TABLE 4. Composition of Aromatic-I (Area %)

		<u>1-Ring</u>	<u>2-Ring</u>	<u>3-Ring</u>
SRC-II	Syncrude	32.0	59.9	8.1
SRC-II	1.5 LHSV	38.6	57.4	4.1
SRC-II	0.5 LHSV	38.5	58.1	3.4
H-coal	Syncrude	28.0	63.0	9.2
H-coal	1.5 LHSV	31.6	63.4	5.0
H-coal	1.0 LHSV	43.1	54.6	2.3

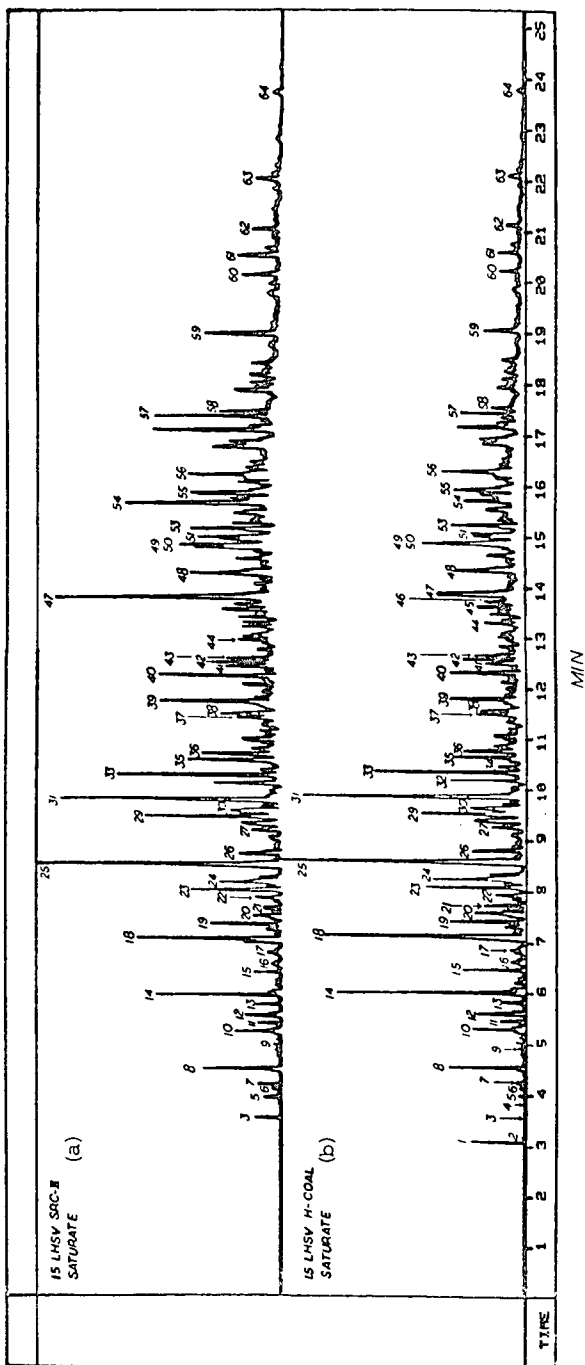


FIGURE 1. GC/MS chromatograms for the saturate fractions of (a) upgraded SRC-II, 1.5 LHSV, and (b) upgraded H-coal, 1.5 LHSV.